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Economics of Sample Compositing as a Screening Tool in Ground Water Quality Monitoring

by R. Rajagopal and L.R. Williams

Abstract

Recent advances in high throughput/automated compositing with robotics/field-screening methods offer seldom-tapped opportunities for achieving cost-reduction in ground water quality monitoring programs. An economic framework is presented in this paper for the evaluation of sample compositing as a screening tool in ground water quality monitoring. When the likelihood of occurrence of a contaminant in a well is very small, the use of sample compositing instead of routine exhaustive sampling will lead to reduction in analytical efforts. Such reduction will be maximum when there are no contaminated wells in the network. An N-fold reduction will result when none of the wells in a network of N wells are contaminated. When 25 percent or more wells in a network are contaminated, the use of sample compositing will require, at the most, an additional 50 percent analytical effort compared to exhaustive sampling. A quantitative measure of the cost-effectiveness of sample compositing as a screening tool is shown to be dependent on two factors: a ratio (f1) of laboratory analytical cost to that of well installation and field sampling costs and a ratio (f2) of the expected number of contaminated wells to that of the total number of wells in the network. Several useful mathematical results of primary interest are derived and illustrated with case examples in the paper. Selected areas for further research are also outlined.

Introduction

Collection and analysis of water, air, food, or soil samples and the interpretation of analytical results are important activities in almost every environmental and health organization. A major share of monitoring dollars is often earmarked for field collection and laboratory analysis of environmental samples. Planned field experiments and collective interpretation of analytical results are crucial to discern spatial and temporal patterns, provide background information, identify violations of standards, evaluate program effectiveness and regulatory compliance, and test various research hypotheses.

Cost-effectiveness criteria have played an important role in the design and development of sampling strategies, especially within some of the major national water and air programs. Many of the publications in this field have dealt with the use of cost-effective resource allocation methods in siting monitoring stations and specifying sampling frequencies, discussion of the pros and cons of fixed stations vs. intensive surveys, and effective utilization of sampling results in episode detection, compliance, and regulation (Beckers and Chamberlain 1974, Chamberlain et al. 1974, Cohen et al. 1975, Minton 1980, U.S. GAO 1981, and Rajagopal 1983).

Traditionally, cost savings in sampling strategies were often accomplished through an understanding of the physical structure of the basin and the processes governing the fate and transport of contaminants within the basin (Sharp 1970, 1971). In the case of man-made contaminants, cost savings can also be effected by incorporating the effluent release patterns of contaminating sources into sampling strategies (Cohen et al. 1975, Rajagopal 1983). Recent advances in laboratory instrumentation and the use of sample compositing procedures offer seldom-tapped opportunities for achieving cost-reduction through sampling design. Compositing is defined as the physical mixing of two or more individual samples to form another sample, which is subsequently analyzed for some parameter. The objective of this paper is to analyze the process of sample compositing as a screening tool in environmental monitoring. Application of this process to ground water quality monitoring at waste sites is illustrated with a generic case study.

Compositing as a Screening Tool

Screening may be defined as the use of rapid and relatively low-cost test methods or procedures to determine whether a characteristic is present or absent (go/no go), present at levels above some threshold value (qualitative), or present in some concentration range (semiquantitative) in a population of values or individuals. Frequently, screening is done to identify where to place the emphasis in subsequent sampling programs, i.e., to gain a preliminary understanding of the system to guide a cost-effective followup required for confirmatory analysis. Screening is being used increasingly in field monitoring programs to minimize the cost of "environmental zeros" (i.e., it helps concentrate on samples containing information about exposure hazard, standard violation, etc. based on the presence of toxicants). In most cases, the cost of chemical

analysis is the same whether or not the compound of interest is detected in the sample. If screening procedures can suggest which samples should be collected to find the parameters of interest, more efficient sampling designs would result. Sample compositing can fit logically into the realm of screening methodology. In fact, the use of compositing is especially attractive in those situations where the likelihood of encountering a parameter of interest is low, i.e., where the cost of "environmental zeroes" is high. In the case of positive analytical results, composite samples can guide in the subsequent sampling and analysis program. The following is a partial list of potential environmental situations in which compositing may be useful:

- Ground water quality sampling at hazardous waste sites and sampling for trace metals in drinking water supplies.
- Soil sampling at hazardous waste sites, where matrix heterogeneity impedes reliable detection.
- Sampling surface water at or near effluent discharging sources.
- Trend analyses to identify the temporal nature of process streams and pollution discharges.
- Human tissue analyses where small sample sizes restrict analytical sensitivity.
- Health surveys where donor confidentiality is a critical factor.
- Contamination of bulk chemical systems, i.e. drums, tanks, etc.

Environmental researchers for a long time have used the process of compositing, both in space and time, as a means of obtaining representative samples. Samples are often taken at different depths across a stream and mixed together to form a composite so as to obtain a better representation of the stream cross section. Similarly, in every type of resource and environmental sampling, compositing is used in an effort to obtain an adequate representation of the population or the universe under study. There have been few publications in the open literature that have dealt with the economics of sample compositing, from multiple sources, used as a screening tool in environmental monitoring.

Experimental designs for environmental monitoring usually have several objectives. Information regarding each individual sample is often obtained by extensive sampling and measurement, while information regarding the sample set as a whole may be obtained by compositing samples and performing fewer analyses. The technique of compositing has been applied to agricultural products (Cameron 1951, Watson 1961, Cassie 1971, Ryan et al. 1982, and Connolly and O'Connor 1982), industrial streams (Sobel and Groll 1959), and geochemistry (Garrett and Sinding-Larsen 1984). Composite sampling reduces the overall cost of analysis, reduces the variance estimate of the average concentration, and, in some cases, increases the probability of detecting toxic chemicals (Mack and Robinson 1985, and Garner et al. 1988).

In general, compositing is recommended (Mack and Robinson 1985) when the following conditions are met:

- Information regarding discrete samples is not important.
- Analytical costs are high relative to sampling costs.
- The probability of detecting the component(s) is low.
- The source identity must be confidential.

Also, in general, compositing is not recommended when the following criteria are met:

- Temporal or spatial information of individual samples is required.
- Composites are reactive or subjected to interference.
- Samples contain highly volatile components that cannot be handled without jeopardizing sample integrity.
- Re-analysis due to limited sample or access is not possible and information is required on discrete "positive" samples.
- The detection limit is near the action level.
- The probability of detection of the analyte or parameter of interest is high.

When samples are composited from multiple sources, the chemistry of the composite may or may not be significantly altered depending on the nature and the composition of individual samples. In many instances, nature itself plays a role in the compositing process through mechanisms such as circulation, dispersion, and diffusion. In other instances, man-made compositing techniques are employed in the field and the laboratory to obtain a better representation of the sampled universe.

In the preliminary discussion of sample compositing as a screening tool in this paper, only conservative contaminants that do not undergo significant transformations in the compositing process are considered. For simplicity, it is assumed that "similar" samples are composited so that the matrix is relatively constant. It is also assumed that the limits of detection are at least one to two orders of magnitude smaller than the required limits of reporting.

An Illustrative Case Study

Factors that influence (or have the potential to influence) ground water quality monitoring decisions at hazardous waste sites include: site and hydrogeological characteristics at the waste facility; technologies related to well design, construction, and operation; quality assurance and quality control procedures associated with field sampling and laboratory analytical methods; sample compositing in the laboratory as a screening tool in monitoring; and the realistic goals of meeting program objectives within a set of resource constraints. There is an extensive body of published literature on these topics, except for the application of sample compositing as a screening tool in ground water quality monitoring. Though sample compositing has wide applicability in environmental monitoring, only its potential as a screening tool in ground water quality monitoring at waste sites is illustrated and discussed in this paper.

A Modeling Exercise

Consider a waste site (and an associated monitoring well network) with very little information on its site characteristics, hydrogeological conditions at its vicinity, and contaminant plume configuration around it, if any. No assumptions regarding the spatial configuration of

wells in the network (their location and depth) are made in this exercise. If a well or wells are contaminated at the site, for the sake of simplicity, it is assumed that each well is equally likely to be contaminated.

One sample is collected from each well for laboratory analysis. Based on the use of sample compositing techniques, certain mathematical expressions are derived for determining the number of required analyses for the detection of contaminated well(s) in a well network. A comparison of the results obtained from such an approach with those of a routine program of sampling all wells in a network is also presented.

Notations and Explanations

N = total number of wells in a network (expressed as 2^k)

k = order of the binary network. For example, networks consisting of a total number of 2, 4, 8, 16, 32, 64 wells are of order 1, 2, 3, 4, 5, 6, respectively.

Total number of wells (N) = $2^{\text{(order of the binary network)}} = 2^k$

For example, $16 = 2^k = 2^4$; order (k) = 4

and $64 = 2^k = 2^6$; order (k) = 6

n = the number of contaminated wells in a network

m = a constant defined by the following inequality

$$2^{(m-1)} \leq n < 2^m. \quad (1)$$

M(n/N) = the number of analyses required to conclusively identify the number n of contaminated wells and the specific wells that are contaminated in a network of N wells.

Using the preceding notations and applying standard enumeration techniques to selected case examples, the following expressions are derived for the number of required analyses.

$$M(n/N) = \begin{cases} 1 & \text{for } n = 0 \\ \sum_{i=0}^{m} 2^i + 2(n)(k-m) & \text{for } 1 \leq n < 2^{(k-2)} \quad (2) \\ \sum_{i=0}^{k-2} 2^i + 2^k & \text{for } n \geq 2^{(k-2)}. \end{cases}$$

In reality, the number of contaminated wells and the identity of specific wells that are contaminated will not be known *a priori*. Therefore, the problem is analyzed in a general fashion and the number of required analyses are derived for a class of worst-case scenarios.

Case of n = 0 (no contaminated well)

Let us consider the case of a 16-well network with no contaminated wells. Analysis of a single sample that has been composited from samples of all the 16 wells will indicate the absence of contamination. Thus, one analysis of a composite sample will be sufficient to determine the absence of contamination, instead of exhaustive analyses of 16 samples, one from each well.

Case of n = 1 (one contaminated well)

Now, consider the same 16-well network with one contaminated well. The process of determining the contaminated well using the technique of sample compositing is illustrated in Figure 1. Figure 1 is essentially a hierarchical representation of sample compositing and the subsequent search process used in identifying the contaminated well(s). At the top of Figure 1 is a composite of 16 samples. As one goes down the hierarchical tree two eight-sample composites, four four-sample composites, eight two-sample composites, and finally 16 individual samples are encountered. The one contaminated sample is shown at the lowest level of the tree. It is the authors' objective to determine the number of analyses required to conclusively identify this sample. As shown in Figure 1, this can be done with nine analyses, which are indicated by an "X" on the hierarchical tree, whereas, a routine method of exhaustive search will require 16 analyses. The process shown in Figure 1 can also be captured by the use of Equation 2 as shown below.

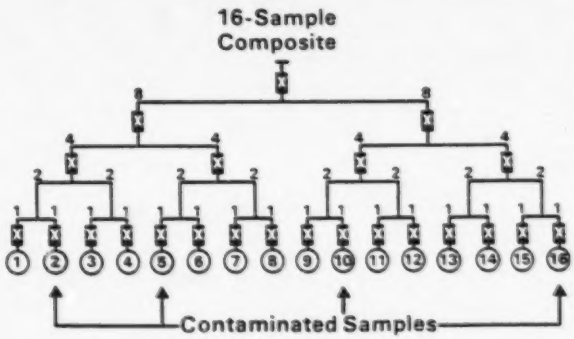

Figure 1. A hierarchical tree diagram of the search process used to identify the one contaminated well (or a sample) in a network of 16 wells. The numbers 16, 8, 4, 2, and 1 at different locations on the tree indicate the number of samples that were mixed to make the corresponding composite or individual sample. Analysis of a sample is indicated by an X below it.

For a 16-well network, we have N = 16 and K = 4 and since one well is contaminated, n = 1. Using inequality (1), it is determined that the value of m is 1 for n = 1. Now, substituting the values of k, n, and m in Equation 2, the following is obtained

$$M(n/N) = \sum_{i=0}^{1} 2^i + 2(1)(4-1)$$

$$= 2^0 + 2^1 + 6 = 9$$

Case of n = 4 (four contaminated wells)

In Figure 2, there is a problem of determining four contaminated samples. If all the four samples were to have been located on a single four-sample composite arm (such as samples numbered 1, 2, 3, and 4; or 9, 10, 11, and 12 in Figure 2), then it would have taken only nine analyses to identify all the four samples. This can be considered the most promising (or the best case) of all scenarios. But in this modeling exercise, the authors have

opted to study only the worst-case scenarios. Hence, to consider the problem in its worst case, the four samples have been dispersed among the four different arms (four-sample composite arms) as shown in Figure 2. This configuration would require 23 analyses, as shown by the number of Xs in Figure 2, to conclusively identify the four contaminated samples. Again, the number of analyses required can be determined using Expressions 1 and 2 as shown below:

We have N = 16, K = 4, n = 4, and since n = 4 is greater than or equal to $2^{(k-2)} = 2^{(4-2)} = 2^2 = 4$, we use the third part of Equation 2 to derive the value of M(n/N), the number of analyses required to identify the four contaminated samples.

$$M(n/N) = \sum_{i=0}^{k-2} 2^i + 2^k = \sum_{i=0}^{4-2} 2^i + 2^4$$

$$= \sum_{i=0}^{2} 2^i + 16 = 2^0 + 2^1 + 2^2 + 16 = 23$$

Notations and Explanations

N = the total number of wells in a network

C_W = capital cost of installing one well at a site with N wells, expressed in present dollars

$A_{i,T}$ = capital recovery factor for a discount rate of 100i percent over T years

$$= \frac{i \cdot (1+i)^T}{(1+i)^T - 1}$$

C_{AW} = annualized capital cost of installing one well at a site with N wells over T years with a discount rate of 100i percent

$= C_W \cdot A_{i,T}$

C_F = prorated cost of field visit, collection, shipping and storage of a single sample (based on N samples)

C_S = prorated cost of laboratory analysis of a single sample for the chosen constituents under study (based on N samples)

R = frequency of sampling/year

p(n/N) = probability of finding n contaminated wells at a site with N wells (to be estimated based on historical data)

M(n/N) = the number of analyses required to conclusively identify the n contaminated wells in an N-well network [as per Equation 2]

E [M(n/N)] = expected value of the number of analyses required to conclusively identify the n contaminated wells in an N-well network

$$= \sum_{n=0}^{N} p(n/N) \cdot M(n/N)$$

$$CCI = \frac{\text{Annual Estimated Cost for an Exhaustive Sampling Program}}{\text{Annual Estimated Cost of a Program Using Sample Compositing}}$$

$$= \frac{\text{(Annualized Capital Costs + Annualized Sampling and Analytical Costs) for the Exhaustive Sampling Program}}{\text{(Annualized Capital Costs + Annualized Sampling and Analytical Costs) for a Program Using Sample Compositing}}$$

$$= \frac{N \cdot C_{AW} + R \cdot N \cdot (C_F + C_S)}{N \cdot C_{AW} + R \cdot N \cdot C_F + R \cdot C_S \cdot E[M(n/N)]} \quad (3)$$

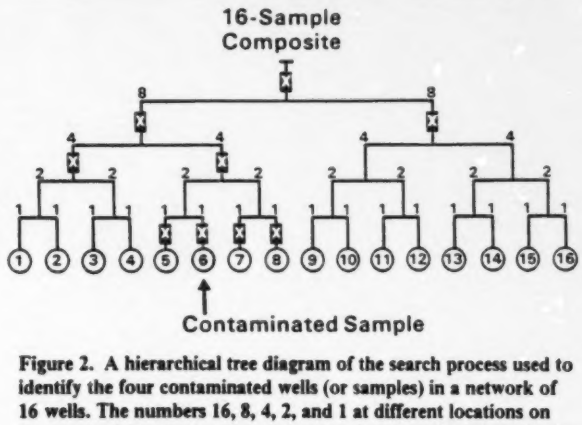

Figure 2. A hierarchical tree diagram of the search process used to identify the four contaminated wells (or samples) in a network of 16 wells. The numbers 16, 8, 4, 2, and 1 at different locations on the tree indicate the number of samples that are mixed to make the corresponding composite or individual sample. Analysis of a sample is indicated by an X below it.

Based on the repeated application of Expressions 1 and 2 for a 16-well and a 32-well network, the number of required analyses for different configurations of contaminated wells is computed and plotted in Figures 3 and 4. When the number of contaminated wells is small relative to the total number of wells in the network, sample compositing can lead to considerable cost savings as shown in Figures 3 and 4. This is often the case with reference to the occurrence of man-made synthetic organic compounds in ground water at hazardous waste sites (Rajagopal 1988). Frequency tabulations of the occurrence of selected organics in ground water samples from waste disposal sites by Gibbons (1987) and Plumb (1985) also show a very large number (or percent) of non-detects or below detection level measurements. In the case of no contamination (the best case), the use of sample compositing will require only (1/N)th of the analytical effort of an exhaustive sampling program for an N-well network. When the number of contaminated wells is greater than or equal to one-fourth the total number of wells in the network, the number of analyses required with sample compositing will be no more than 1.5 times the number of analyses required under a plan of exhaustive sampling (as in Figures 3 and 4). Therefore, sample compositing, even in the worst case, will not require any more than 1.5 times the analytical effort expended in an exhaustive sampling program. In addition, comparison of values obtained with composites to those of discrete samples can help confirm or reject extreme analytical results and thereby serve as a quality control tool.

A Comparative Cost Analysis

In this section the authors derive an expression for a

comparative cost index (CCI). The index compares the estimated annual cost of an exhaustive sampling program with that of a program using sample compositing for a network of N wells. For ease in analysis, a variety of simplifying assumptions are made and an illustrative case example is presented.

An Example

Consider a site with a 16-well network, an estimated probability distribution p(n/N), and the number of analyses M(n/N) required to conclusively identify the n contaminated wells [derived from Equation 2] as per data presented in Table 1 below:

TABLE 1

n	p(n/16)	M(n/N)	p(n/N)·M(n/N)
0	0.60	1	0.60
1	0.20	9	1.80
2	0.10	15	1.50
3	0.04	19	0.76
4	0.03	23	0.69
5	0.02	23	0.46
6	0.005	23	0.115
7	0.003	23	0.069
8-16	0.002	23	0.046
E [M(n/N]			6.04

To illustrate the computation of CCI, the following estimates are used:

$N = 16$; $C_W = \$1000$; $A_{(0.10,10)} = 0.1627$; $C_F = \$100$; $C_S = \$1000$; and $R = 1$.

Substituting the preceding estimates in Equation 3 for CCI, we have

$$CCI = \frac{16\,(1000)\,(0.1627) + 1\,(16)\,(100) + 1\,(16)\,(1000)}{16\,(1000)\,(0.1627) + 1\,(16)\,(100) + 1\,(6.04)\,(1000)}$$

$$= \frac{2603 + 1600 + 16{,}000}{2603 + 1600 + 6040}$$

$$= \frac{20{,}203}{10{,}243}$$

$$= 1.97\ .$$

What these computations reveal is that for the preceding specifications, sample compositing is 1.97 times more economical than a program of exhaustive sampling of wells at the site. Equation 3 can be rewritten in a more elegant form as follows:

$$CCI = \frac{N \cdot C_{AW} + R \cdot N \cdot C_F + R \cdot N \cdot C_S}{N \cdot C_{AW} + R \cdot N \cdot C_F + R \cdot E[M(n/N)] \cdot C_S}$$

$$= \frac{1 + f1}{1 + f1 \cdot f2} \qquad (4)$$

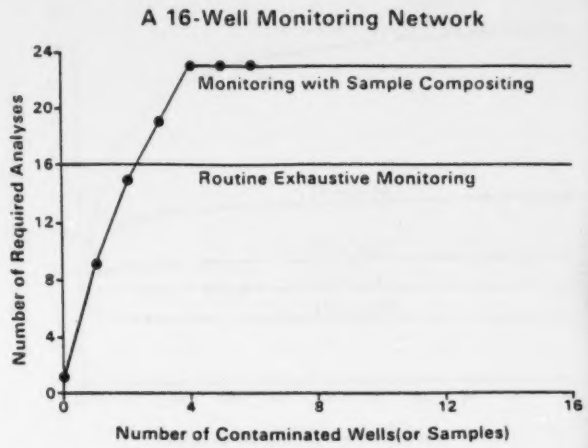

Figure 3. The number of analyses, using sample compositing, required to conclusively identify the contaminated wells in a network of 16 wells is plotted against all possible numbers of contaminated wells. The 16 analyses required for routine exhaustive monitoring are plotted as a straight line.

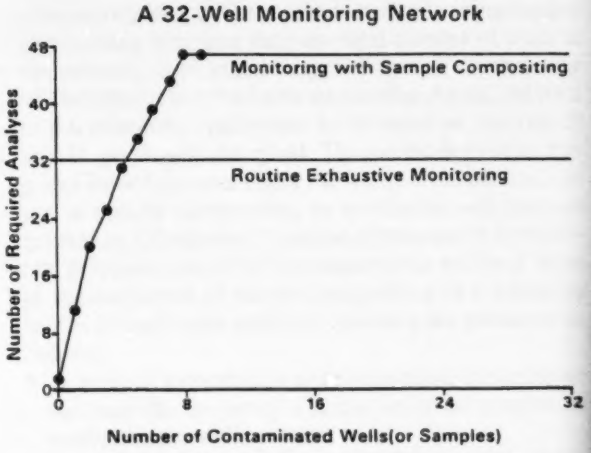

Figure 4. The number of analyses, using sample compositing, required to conclusively identify the contaminated wells in a network of 32 wells is plotted against all possible numbers of contaminated wells. The 32 analyses required for routine exhaustive monitoring are plotted as a straight line.

where, $f1 = \frac{R \cdot C_S}{C_{AW} + R \cdot C_F}$ and $f2 = \frac{E\,[M(n/N)]}{N}$.

f1 is a ratio of prorated yearly analytical cost of a single sample to that of the sum of the annualized cost of a single well and prorated yearly cost of field visit, sample collection, shipping, and storage for a single sample. In other words, f1 is a ratio of annualized variable cost to that of annualized fixed costs. f2 is a ratio of the expected value of the number of analyses required to conclusively identify the contaminated wells using sample compositing to that of the total number of wells in the network, which is the same as the number of analyses required under an exhaustive monitoring program. Figure 5 captures the essence of Equation 4 in a graphical form. The values of CCI are plotted for several different combinations of f1 and f2. The results can be summarized as follows:

$$
\text{CCI} \rightarrow \begin{cases} \text{a) } 1/f2 & \text{for } 0 < f2 < 1 \text{ and } f1 >>>> 1 \\ \text{b) } 1^{+} & \text{for } 0 < f2 < 1 \text{ and } f1 <<<< 1 \\ \text{c) } 1 & \text{for } f2 = 1 \text{ and all } f1 \\ \text{d) } 1^{-} & \text{for } 1 < f2 < 1.5 \text{ and } f1 <<<< 1 \\ \text{e) } 1/f2 & \text{for } 1 < f2 < 1.5 \text{ and } f1 >>>> 1 \,. \end{cases} \quad (5)
$$

From the first Expression 5a in the preceding system, it can be seen that for f1 significantly larger than 1 and f2 less than 1, CCI asymptotically approaches the value 1/f2. In short, if prorated sample analytical cost is significantly higher than the sum of the prorated (or annualized) well installation and field sampling costs, then CCI will approach a value 1/f2.

Again, as shown in Expressions 5a and 5b, for all f2 less than 1, CCI is greater than 1, indicating the economic superiority of using sample compositing as a screening tool in monitoring. When f2 is equal to 1 as in (5c), CCI is equal to 1 irrespective of the value taken by f1. Under this case both approaches, sample compositing and exhaustive monitoring, will cost the same. Finally, in the case of f2 greater than 1 as in (5d) and (5e), CCI is less than 1, thus indicating the economic inferiority of using sample compositing as a screening tool in monitoring. In the asymptotic case of (5e), where f1 is considerably larger than 1, CCI approaches 1/f2. Because f2 can never be greater than 1.5 (as shown in Figures 3 and 4), CCI can never be less than 1/1.5 or 2/3. In short, even under the worst of conditions, the use of sample compositing as a screening tool will cost no more than 150 percent of the cost of exhaustive monitoring.

Conclusions and Notes on Further Research

An economic framework for the analysis of sample compositing as a screening tool in ground water quality monitoring is presented. The framework developed in this paper can be readily applied to a class of conservative contaminants that do not undergo significant changes in the compositing process. Further, it is assumed that the detection limit of the instrument used to analyze the contaminant(s) is of at least 1 to 2 orders of magnitude smaller than that of the needed reporting requirements.

Based on a modeling exercise, it is shown that sample compositing can lead to considerable savings in analytical effort when the number of contaminated wells is small relative to the total number of wells in the network. The benefits of sample compositing are maximum when there are no contaminated wells in the network. When 25 percent or more wells in the network are contaminated, sample compositing will require at the most 50 percent additional analyses compared to a corresponding program of exhaustive monitoring of wells in the network.

The economic analysis presented in this paper shows that the use of sample compositing in monitoring can be superior to exhaustive monitoring whenever the expected value of the number of analyses required to conclusively identify the contaminated wells using compositing is smaller than the total number of wells in the network. The level of this superiority is governed by two factors f1 and f2, which in turn are determined by a ratio of costs (variable to fixed) and the frequency distribution of contaminated wells at waste sites (as per Equation 4). If the expected value of the number of analyses required to conclusively identify the contaminated wells using sample compositing is greater than the total number of wells in the network, then monitoring with sample compositing will be inferior to exhaustive monitoring. Again, the level of this inferiority is governed by the same two factors, f1 and f2, previously described. The results derived in this paper show that even under the worst of conditions, the use of sample compositing in monitoring will cost no more than 150 percent of the cost of exhaustive monitoring. Selected areas of further research that will be of value in the evaluation of sample compositing as a screening tool in ground water quality monitoring are presented as follows:

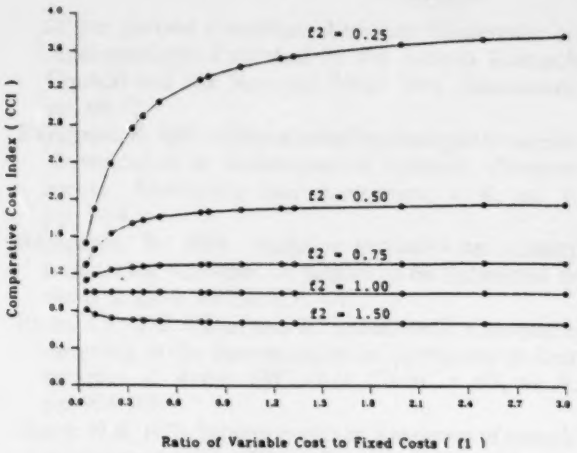

Figure 5. The Comparative Cost Index (CCI) given by Equation 4 is plotted for a range of values of f1 (0.05, 0.10, 0.20, 0.33, 0.40, 0.50, 0.75, 0.80, 1.00, 1.25, 1.33, 2.00, 2.50, 3.00), and f2 (0.25, 0.50, 0.75, 1.00, 1.50).

- A study of hazardous waste sites around the nation to estimate the frequency distribution of the number of contaminated wells per site.
- Laboratory analyses of a variety of composites generated by mixing samples of known quality (standards) could be used to determine the conditions under which sample compositing can be used as a screening tool in monitoring. This process would help identify the potential chemical transformations that may result from the compositing process.
- Site characterization (hydrogeological information and well-placement capability) and its impact on the results of economic analysis presented in this paper.
- Possible uses of the methods presented in this paper for the justification of investments in more expensive but higher resolution (lower detection limits) analytical instruments.

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Notice

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